Application of the thiourea isomerization to ethyl hydrogen maleate failed to yield the corresponding fumarate, suggesting limitation of the isomerization to methyl hydrogen maleate.

Although mineral acids[2] are also known to invert maleic acid, the choice of the relatively neutral thiourea for methyl hydrogen maleate is advantageous in avoiding or minimizing the possibilities of hydrolysis and of disproportionation to fumaric acid and dimethyl fumarate.

Hitherto, methyl hydrogen fumarate has been prepared by the partial saponification of dimethyl fumarate,[3] from fumaryl chloride, methanol, and water,[4] and by the oxidation of methyl sorbate.[5] Our inversion of methyl hydrogen maleate, as a preparative method for the fumarate, is characterized by simplicity and ease of isolation of the product. The over-all yield of the two-step synthesis is 74% of theory.

EXPERIMENTAL

Methyl hydrogen maleate. A 2-liter, three-necked flask, fitted with an agitator, thermometer, dropping funnel, and a reflux condenser topped by a sodium sulfate drying tube, was charged with 980 g. (10.0 moles) of maleic anhydride (hood!). The dropping funnel was charged with 320 g. (10.0 moles) of anhydrous methanol and 10–15% of the alcohol was added to the reaction flask. The mixture was heated on a water bath to 50–55°, and stirred by hand until the maleic anhydride was in solution. The remainder of the alcohol was added under mechanical agitation over a period of 1–2 hr., keeping the temperature at 50–55°. After the addition was completed the agitated solution was held at 50–55° for one more hour, cooled to room temperature, and bottled without further treatment. The yield of methyl hydrogen maleate (n_D^{20} 1.4634, d_4^{20} 1.2520) was quantitative.

Anal. Calcd. for $C_5H_6O_4$: neut. equiv., 130.0; MR_D, 28.0.[6] Found: neut. equiv., 129.5; MR_D, 28.6.

Methyl hydrogen fumarate. Six grams of thiourea was added to a stirred solution of 125 g. (0.96 mole) of methyl hydrogen maleate in 125 g. of water. After 3.5 hr. of agitation at room temperature, the mixture was cooled to 5° and centrifuged at 2500 r.p.m. in a porcelain basket. The white, voluminous precipitate of methyl hydrogen fumarate was washed three times with 100-ml. portions of ice water, and centrifuged once more for 20 min.

To the combined first filtrate and first two washes was added 5 g. of thiourea, and the solution stirred for an additional 12 hr. at room temperature. After cooling, the isolation procedure was repeated. The combined precipitates were dried in a vacuum oven at 50°. The yield was 93 g. (74.6%) and the m.p. of 142–144° compared favorably with the previously reported values[4,7–9] of 143° and 144.5°. Our product is 95.4% pure; it is contaminated with 4.6% fumaric acid, as determined by the alkali titration (calcd. neut. equiv., 130.0; found neut. equiv., 123.5).

Ethyl hydrogen maleate.[10] Four hundred and sixty grams (10.0 moles) of anhydrous ethanol, previously dried further by refluxing over calcium oxide, was reacted with 980 g. (10.0 moles) of maleic anhydride in the manner described for the preparation of the methyl half-ester. The yield of product (n_D^{20}, 1.4560; d_4^{20} 1.1760) was quantitative.

Anal. Calcd. for $C_6H_8O_4$: neut. equiv., 144.0; MR_D, 32.6.[6] Found: neut. equiv., 141.7; MR_D, 33.3.

Attempted isomerization of ethyl hydrogen maleate. The action of 5 g. of thiourea on a stirred solution of 100 g. (0.695 mole) of ethyl hydrogen maleate in 100 g. of water for 72 hr. failed to yield detectable quantities of the water-insoluble ethyl hydrogen fumarate.

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Deamination of 2,2,3,3-Tetrafluorocyclobutanemethylamine

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The Demjanow rearrangement of cycloalkanemethylamines to produce the corresponding ring-enlarged alcohol on treatment with nitrous acid has been successfully applied to rings containing three to eight carbon atoms.[1,2,3] The presence of a halogen atom on the ring appears to prevent ring expansion. In the one case reported,[4] 2-chlorocyclohexanemethylamine was found to give only the corresponding unrearranged alcohol under conditions normally leading to ring expansion of the unhalogenated ring. Elphimoff-Felkin and Tchoubar[5] have shown that in certain cases cyclopentane rings will show ring expansion where the corresponding cyclohexane compounds will not. This is presumed due to the relative ease of formation of the six- versus seven-membered ring.

In the course of another investigation, 2,2,3,3-tetrafluorocyclobutanemethylamine, I, was prepared by the cyclodimerization of acrylonitrile and tetrafluoroethylene followed by catalytic hydrogenation of the carbonitrile. It was expected that on deamination relief of ring strain would provide sufficient

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driving force for ring expansion even in the presence of the electronegative groups.

Treatment of the amine, I, with nitrous acid under modified Demjanow conditions[6] resulted in a 69% yield of an alcohol fraction and <5% unidentified olefins. A small amount of the starting amine was recovered as the benzamide. The alcohol fraction was identified as consisting of >95% unrearranged alcohol, 2,2,3,3-tetrafluorocyclobutanemethanol, II. None of the expected ring-enlarged product, tetrafluorocyclopentanol, was obtained. The alcohol fraction was identified by NMR and comparison of the physical properties and derivatives with those of an authentic sample of II, prepared by the cyclodimerization of tetrafluoroethylene and allyl alcohol.[7]

This is the first example in which a simple cyclobutanemethylamine has failed to show ring enlargement on deamination.

EXPERIMENTAL

2,2,3,3-Tetrafluorocyclobutanecarbonitrile. This compound was prepared according to the method of Coffman[7] from acrylonitrile and tetrafluoroethylene. The fraction having a b.p. 72–73.5° (50 mm.) was collected.

2,2,3,3-Tetrafluorocyclobutanemethylamine, I. A mixture of tetrafluorocyclobutanecarbonitrile (46.8 g., 0.3 mole), acetic anhydride (33 g., 0.33 mole), anhydrous ethyl ether (90 ml.), and PtO_2 (2.0 g.) was placed in a hydrogenation bomb. The bomb was pressured to 1000 p.s.i.g. with hydrogen and the temperature was slowly raised while agitating. At 60°, the pressure dropped to 500 p.s.i.g. in 10 min. The bomb was repressured to 1000 p.s.i.g. and held for 2 hr. at 60°. The final pressure was 850 p.s.i.g. The cooled reaction products were filtered to remove the catalyst and the excess ether and acetic anhydride were removed under vacuum to yield a viscous oil (62.3 g.). The oily product, believed to be an acetyl derivative, was refluxed for 6 hr. in 30% sulfuric acid. The hydrolysis mass was cooled and made slightly alkaline with sodium hydroxide and extracted with three 100-ml. portions of ether. The combined ether portion was dried over potassium hydroxide pellets. Some decomposition occurred in the drying step as evidenced by considerable darkening of the ether solution. The ether solution was decanted from the potassium hydroxide and distilled through a 36-in. spinning band column. The amine, b.p. 43–45° (20 mm.), was isolated as a colorless oil in a 30% over-all yield from the nitrile.

Anal. Calcd. for $C_5H_5F_4N$: C, 38.3; H, 4.46; N, 8.9. Found: C, 38.3; H, 4.85; N, 8.7.

The benzamide was prepared and formed white plates from aqueous ethanol, m.p. 92.0–92.5°.

Anal. Calcd. for $C_{12}H_{11}F_4NO$: C, 55.1; H, 4.2; N, 5.4. Found: C, 55.7; H, 4.3; N, 5.6.

Deamination of I. To a solution of I (10.0 g., 0.064 mole) and monobasic sodium phosphate (35 g., 0.25 mole) in 150 ml. water was added a solution of sodium nitrite (4.5 g., 0.065 mole) in 10 ml. of water. The resulting mixture was heated at reflux for 4 hr. Nitrogen was evolved and a brown oil formed on the surface. The oil layer was extracted with three 30-ml. portions of ether; the ether portions were combined, dried, and distilled. A small forerun, b.p. 87–153°, was obtained and the main fraction, 5.8 g., distilled at 153–155°. Some decomposition occurred in the pot and the residue amounted to 1.1 g. A small amount of unreacted amine (0.2 g.) was recovered from the aqueous solution as the benzamide. The *p*-nitrobenzoate of the alcohol fraction was prepared and formed white needles from aqueous ethanol, m.p. 90–91°.

Anal. Calcd. for $C_{12}H_9F_4NO_4$: C, 47.0; H, 2.9. Found: C, 47.3; H, 3.0.

An authentic sample of 2,2,3,3-tetrafluorocyclobutanemethanol was prepared according to the method of Coffman,[7] from tetrafluoroethylene and allyl alcohol. The product, b.p. 155–156° (760 mm.), had an identical infrared spectrum with the deaminated product from I with the exception of a minor band at 5.95 microns. This band could be due either to carbonyl or an unsaturated fluorine compound present to a small extent in the deaminated product.

The *p*-nitrobenzoate of the known alcohol melted at 90–91° and showed no depression on admixture with the derivative of the deaminated product.

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Reduction of Carbonyl Compounds with Pyridine Borane

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The reduction of various carbonyl compounds with pyridine borane to the alcohol stage has been studied qualitatively. This reagent reduces aldehydes and ketones (chiefly aromatic) in yields ranging from 24% to 94%; acids and acid chlorides in yields ranging from 21% to 40%. All attempts to reduce esters and salts of carboxylic acids failed.

The reduction of carbonyl compounds with various hydrides has been the subject of several investigations.[2–4] Such an investigation has been carried out in this laboratory with pyridine borane, one of the several known borine complexes.

Pyridine borane was first prepared by Schlesinger and co-workers,[5] by the reaction of diborane and pyridine using vacuum techniques. A more convenient synthesis was developed by Taylor and associates,[6] using anhydrous pyridine hydrochloride and sodium borohydride in pyridine as the solvent.

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